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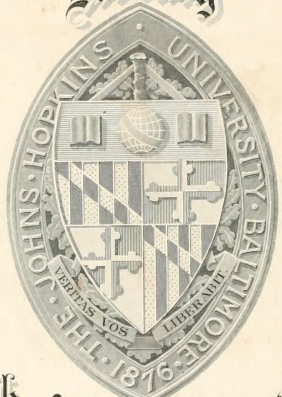

of the
Johns Hopkins University

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W. R.
1887
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ON THE

Diazo Alcohol Reaction.

DISSERTATION

Presented for the Degree

OF

Doctor of Philosophy

AT THE

Johns Hopkins University,

BY

W. R. Orndorff, A.B.

1887.

54 438

The Diazo Alcohol Reaction

William R. Orndorff, A.B.,
Baltimore,
Maryland

The work described in this paper was carried on in the chemical laboratory of the Johns Hopkins University, during the scholastic years 1885-1886, and 1886-1887, under the direction of Professor Remsen. For the aid and encouragement, which I have at all times received from him, I desire here to express my deepest gratitude. If in this work any light has been shed on the problem investigated, it is entirely due to the teaching of Professor Ira Remsen.

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[illegible] [illegible]

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Introduction.

In his famous investigation on the diazo compounds, published in 1866, Griess states, that the principal products obtained in the decomposition of diazo-benzene nitrate or diazo-benzene sulphate in alcohol, is benzene. This decomposition he represents by these two equations:

$C_6H_4N_2NHO_3 + C_2H_6O = C_6H_6 + C_2H_4O_2 + N_2 + HNO_2$

Nitrobenzamide alcohol. Benzoic aldehyde.

$C_6H_4N_2SH_2O_4 + C_2H_6O = C_6H_6 + C_2H_4O_2 + N_2 + H_2SO_4$

Diazobenzene sulphate - alcohol Benzene aldehyde.

This reaction was regarded as a general one for the replacement of the amido group by hydrogen, and no exception to it was recorded until 1870, when E. Mroblewsky[2] while working with the two isomeric

[1] Annalen 137, 65 & 67. [2] Zeit. f. Chem. 6, 164 & Berichte 3, 98.

$C_6H_3\begin{cases}CH_3\ (1)\\NH_2\ (2)\\Cl\ (4)\end{cases}$ and $C_6H_3\begin{cases}CH_3\ (1)\\NH_2\ (3)\\Cl\ (4)\end{cases}$?

found, that when he attempted to convert them into the chlortoluenes by the Sandmeyer diazo reaction, he obtained the other isomers of the [illegible] i.e. 1) [illegible] monochlor-methyl-phenetol, He represents the reaction — by the equation:

$C_7H_6ClN_2HSO_4 + C_2H_6O = C_7H_7ClO + N_2 + HSO_4$

Ethyl chlorcresol

and calls attention to the fact that it forms an exception to the [illegible] Reaction. Hoffmeister[1] in 1871 records the formation of dichlor-[illegible] by the action of [illegible] upon diazo-[illegible] prepared by the [illegible] process.

[1] Ann. [illegible]

$C_6H_5N_2HSO_4 + C_6H_5OH = \begin{matrix} C_6H_5 \\ C_6H_4 \end{matrix} > O + H_2SO_4 + N_2$

The yield was, however, very small only about 0.5% of the theoretical. Meyer and Stüber[1] in 1873 found that, action of ethyl nitrite on benzamide, the ether of benzoic acid [illegible], and not benzoic aldehyde as they had expected. This reaction they represent thus:

$C_6H_5CONH_2 + NO.OC_2H_5 = N_2 + H_2O + C_6H_5COOC_2H_5$

Benzamide — Ethyl benzoate

They comment on the difference in conduct of the amido group towards ethyl nitrite, according as it is joined to phenyl, C_6H_5, benzoyl, C_6H_5CO, or ethyl, C_2H_5.

oder a very small quantity of Fuyse, was exactly converted into a dark resin. Hauduck[1] in 1874 calls attention to the formation of an ethyl cresol sulphonic acid (from (o) amido (p) toluene sulphonic acid by the decomposition of the diazo compound; [illegible] the result as follows:

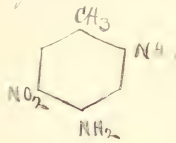
$$C_6H_3\begin{cases}CH_3\ (1)\\ N\equiv N\ (2)\\ SO_3H\ (4)\end{cases} + C_2H_5OH = C_6H_3\begin{cases}CH_3\ (1)\\ OC_2H_5\ (2)\\ SO_3H\ (4)\end{cases} + 2N.$$

He also obtained meta cresol sulphonic acid [illegible] by [illegible]

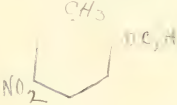
Ladenburg[2] in 1875 obtained a compound, soluble in alcohol, by treating an alcoholic solution [illegible] with a mineral acid and nitrogen trioxide. (N

[1] Annalen 172, 205. [2] Berichte 1875 8 1212

Taking the reaction solution, in which the diazo compound was formed, nitrogen [illegible], and he obtained as ether ether of nitro cresol. The structure of this nitrotoluylene diamine as shown by Staedel[1] is represented by the formula:



and the ether ether of nitro cresol according to Staedel by the formula:



This case is then exceedingly interesting because both the normal (Griess) and the abnormal (phenetol) reaction here take place in the same molecule under exactly the same

1/ Annalen 217, 155 (footnote)

condition. It proves to be the para position to methyl being replaced by hydrogen, [illegible] the ortho to methyl is preferentially [illegible] the [illegible] group.

Tiffeneau is the first to record with this peculiar diazo-alcohol reaction. In 1871 he found that the sulphate of the base resulting from reducing the nitro-ortho-toluic acid, made by the nitration of [illegible] with yellow nitrobenzoic acid, when boiled with alcohol gave off [illegible] acid, equivalent to the [illegible]:

$$C_6H_4 \begin{cases} COOH \\ NH_2 \cdot H_2SO_4 \end{cases} + C_2H_5OH = C_6H_4 \begin{cases} COOC_2H_5 \\ OH \end{cases} + N_2 + H_2SO_4$$

and not benzoic acid, as he had expected. The meta amido benzoic acid [illegible] corresponding to tiffeneau acid [illegible]

[illegible] 11/12-09

[illegible] acid, [illegible] acid, [illegible] acid, [

Thus:

$$C_6H_3\begin{cases}N{=}N(m)\\SO_3\\SO_3K\end{cases} + C_2H_6O = C_6H_3\begin{cases}OC_2H_5\text{-}(m)\\SO_3H\\SO_3K\end{cases} + 2N.$$

Balentine[1] in 1910 failed to get the regular diazo alcohol reaction by heating the diazo compound of hydrazo-benzene-sulphonic acid with absolute alcohol in den. increased pressure at 110° C. He seems unable to obtain a crystalline product, but his analysis of the impure substance corresponds with the [illegible] compound.

Norris and Brewer[2] in 1912 obtained a good yield of the above substance by heating the diazo compound from sulphanilic acid with absolute alcohol. The equation given by them

[illegible] 202, 337. [2] Am. Chem. Journ. 44, 374

with the one already described by Hausbrand. He explains the formation [illegible] as follows:

The (o) amido (p) toluene sulphamide is first converted by the assumption [illegible] into the amido-toluene sulphonic acid,

$$C_7H_6\begin{cases}NH_2\,(o)\\SO_2NH_2\end{cases} + H_2O = C_7H_6\begin{cases}NH_2\\SO_3H\end{cases} + NH_3.$$

This amido toluene sulphonic acid is then converted into the diazo- [illegible] oxide

$$C_7H_6\begin{cases}NH_2\,(o)\\SO_3H\end{cases} + HNO_2 = C_7H_6\begin{cases}N\\\|\\N\\O\end{cases} + 2H_2O$$

This diazo compound then decomposes with the alcohol, yielding the ethoxy-para toluene sulphonic acid.

$$C_7H_6\begin{cases}N=N\,(o)\\SO_3H\end{cases} + C_2H_5OH = C_7H_6\begin{cases}OC_2H_5\,(o)\\SO_3H\end{cases} + N_2$$

[illegible]

[illegible]

[illegible]

[illegible]

$$C_2H_5J + Ag_2O = AgJ + C_2H_5OH$$

[illegible]

[illegible]

[illegible]

[illegible]

$$C_6H_5ONa + C_2H_5J = NaJ + C_6H_5OC_2H_5$$

Hallerly in 1884 obtained the monomethyl ether by decomposing bromo-

[illegible]

Cumene sulphate, made from crystallized Cumidine, with absolute alcohol under a pressure at 100 m.m. we represent this reaction as follows:

$$C_6H_2(CH_3)_3 - N=N.SO_4H$$
$$OC_2H_5 \quad H$$

Hallen also finds that the diazo compounds of other bases besides Cumidine, [illegible] composition with alcohol. The diazobenzine sulphate gave phenyl [illegible], diazo-naphthalene sulphate gave principally β-naphthol ethyl ether,

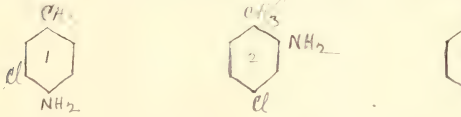
$$C_{10}H_7OC_2H_5,$$

also formed at the same time.

Hofmann[illegible] in 1858 obtained the [illegible]

E. Wróblewski // in 1884 calls attention
previous work, [illegible]

which he had obtained on the diazo alcohol reaction. He made three isomeric chlortoluidines, having the structures represented by the following formulae:



These chlortoluidines were then converted into the corresponding diazo salts and these diazo compounds [illegible]. They decomposed in accordance with the equation

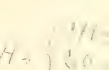
$$C_6H_3Cl(CH_3)N_2.HSO_4 + C_2H_6O = C_6H_4Cl(CH_3) + C_2H_4O + H_2SO_4 + N_2,$$

Metachlortoluene being obtained. The diazo compounds corresponding to the second and third chlortoluidine yielded on decomposition the isomeric monochlormethylphenols according to the equation:

$C_7H_6ClN_2HSO_4 + C_7H_7\text{-}OH = C_7H_6ClO\,C_7H_7 + N_2\,|\,H_2SO_4$

[illegible] these results that
decomposition of the diazo
compound in the presence of the normal
reaction suffers a change due to
the influence of the halogen —
the hydrogen thus
displaced enters
occupies the para-position
active to some second substituent
group."

Remsen and Palmer[11] in 1890 found
that the diazo compound, made from
o. chloro toluene sulphonic acid,



[illegible]

[illegible] acid [illegible] the
[illegible] the
formation [illegible] the [illegible]
[illegible] the
diazo compound,

$$C_6H_3\text{-}SO_3H.\left\langle \begin{matrix} SO_3 \\ N \end{matrix} \right\rangle N(0),$$

[illegible] the toluidin- disulpho-
[illegible] acid, $C_6H_2(CH_3)(NH_2)(SO_3H)(SO_3H)$,
with absolute alcohol under a
[illegible]

$$C_6H_2(CH_3)(CH_3)(SO_3H)(SO_3H)$$

Xylidine [illegible] acid,

$$C_6H_2(CH_3)(CH_3)(NH_2)(HSO_3),$$

[illegible]
which on boiling with absolute

[illegible] Berichte 18, 2176, 2184, 2185.

alcohol under a pressure of 200 m.m.
gave an ethoxy xylene sulphonic
acid

$C_6H_2(CH_3)(CH_3)(OC_2H_5)(SO_3H)$

The [illegible] compound [illegible]

$C_6H_2(CH_3)(NO_2)(NH_2)(HSO_3)$,

with alcohol and sodium gave
the ethoxy compound

$C_6H_2(CH_3)(NO_2)(OC_2H_5)(HSO_3)$

The [illegible] prepared from

$C_6H(CH_3)(CH_3)(CH_3)(NO_2)(NH_2)(SO_2H)$

alcohol, treated with alcohol & sodium
it gave the ethoxy compound,

$C_6H(CH_3)(CH_3)(CH_3)(NO_2)(OC_2H_5)(SO_2H)$.

Reasons and [illegible]
of the amido compounds, which
have been found to give the
[illegible]
[illegible]

widely from one another in character, undergo this peculiar transformation and there is no common feature presented by all of them which suggests an explanation. This is even true, if except the fact, that of the 24 amido compounds above mentioned, 19 contain paraffin residues and of these 19 compounds 11 contain the paraffin group and the amido group in the ortho position relative to each other. It may

Diazo-Benzene Nitrate

The diazo benzene nitrate was made according to the method of Griess, as follows: Pure aniline nitrate was first made and ground to a fine powder. Then 20 grams of the powder were then placed in a 200 c.c. florence flask, mixed with distilled water, 40 to 50 c.c. to each gram, and placed in an ice water bath and a current of nitrogen dioxide passed through the mass. The flask must be shaken constantly in order to prevent the temperature from rising and decomposing the diazo compound. The aniline nitrate soon dissolves and is completely converted to diazo-benzene nitrate, water

of absolute alcohol, which has been previously cooled down to 0°C, and

$$C_6H_4\begin{cases}NO_2\\OH\end{cases} + HNO_3 = C_6H_3\begin{cases}(NO_2)_2\\OH\end{cases} + H_2O.$$

21 grams of ortho nitro-phenol were obtained as in 10 grams of dinitro-phenol, which is equivalent although to 21 grams of orthoamino-phenol, hence the yield of ortho nitro-phenol formed according to the above equation is 13% of the theoretical. Of the 260 grams of diazo benzene nitrate used

22% decomposed yielding Phenol
13% " " Nitrophenol
4% " " Diazoamine

It is thus evident from the

chairman, that in the decomposition of diazo-organic nitrates by alcohol, the principal reaction is that with phenetol, and not as is generally stated, with benzene, though both reactions take place side by side. The action of alcohol on diazo-benzene nitrate is then entirely analogous to the action of water, as is shown by the equation:

$C_6H_5-N_2NO_3 + HOH = C_6H_5-OH + HNO_3 + N_2$

$C_6H_5N_2NO_3 + C_2H_5OH = C_6H_5OC_2H_5 + HNO_3 + N_2$

The reaction with water giving

and benzene was very small,

Dear Cooper [illegible]

After many months [illegible]
[illegible] I [illegible]
[illegible] the [illegible]
[illegible] [illegible]
[illegible] [illegible]
[illegible]

after the addition of each drop
to prevent the milk from curdling
and thereby preventing the
drop from sinking after coming
in contact with the milk, the mixture
is again stirred, and then
poured into test tubes. The tubes
of mixture are placed in a
test tube rack. Each of the
test tubes contains about two cubic
centimeters of mixture and is
then placed in the bottom of the
glass jar. The water will now
cover the test tubes and the
mixture in the test tubes. The
jar is then covered with
cheese cloth and the water

the mixture [illegible] from
brown, which [illegible] over a day
exposed to the light. All the
diazo benzene sulphate used
was [illegible] and dried according to the
method.

Action of Hydrazine on Diazo-benzene Sulphate.

The method [illegible]
[illegible]
mass of the crystals, [illegible] 20 grams
diazo benzene sulphate
heated in a two litre balloon
flask, 200 c.c. absolute (99.7%)
alcohol added, the reaction
[illegible]
[illegible]

on a water bath. The solution began at first to boil (temperature, 115°). It began to decompose slowly, but no odor of aldehyde could be detected during the entire reaction. The solution in the flask was finally heated for 3 hours, to insure the complete decomposition of the diacetal.

150 grams of the liquid contents of the flask were then subjected to fractional distillation according to the usual method, and the following results obtained:

Portion of the 3 grams of dimethylacetal used, passed over at 64°, and the remainder distilled off from 64° to 100°. This latter distillate, which did

mate [illegible] aldehyde, [illegible]
[illegible] mixture was cooled, was
diluted with five times its
volume of a saturated solution
of common salt, and allowed
to stand. [illegible]
place in the [illegible] of the liquid.
[illegible] was separated, washed with
[illegible] solution [illegible] and dried
dried over fused calcium chloride.
Subjected to fractional distillation
and obtained 2 grams
of a liquid boiling at 70° to 74°. This
solidified on [illegible] to 0°, [illegible]
[illegible] and boiled constantly at 80° to 81° in the [illegible]
[illegible] fraction, boiling at 77° to 78° was found
to be [illegible]
Water is also added to the [illegible]
residue, kept on the [illegible] after

distilling off the alcohol, and the mixture subjected to distillation in steam. With the steam goes over a liquid, which has a pleasant odour like oil of bitter almonds. It is then treated with dilute sulphuric acid, and distilled. The oil, the yield of which is about 70 per cent, boils at 170° and, when further rectification is found to be necessary, is treated with ferrous carbonate, which takes up the hydrocyanic acid, and the oil then distilled over again separately to dryness. The oil will keep in the dark

which was benzene-azo-sulphate, produced by the action of the nitro-sulphuric acid on the benzene.

The products of the action of alcohol on diazo-benzene sulphate are then:

(1) Phenetol,

(2) Benzene.

In the case of the nitrate we have, as we should expect, the formation of nitro-phenetol, but, strange to say, the most important, the main product according to the equation,

$C_6H_5-N_2HSO_4 + C_2H_6O = C_6H_5-OC_2H_5 + H_2SO_4 + N_2$

and secondly, the one to which benzene is produced,

$C_6H_5-N_2HSO_4 + C_2H_6O = C_6H_6 + C_2H_4O + H_2SO_4 + N_2$.

H_2O present of phenetol [illegible]

-pared with absolute alcohol,
[illegible] and with Griess,
as originally stated by Griess.
In connection with these results
with [illegible]
[illegible]
can [illegible]
secured, it would be mentioned related
results, (see page 13), with β naphthyl-
amine, the simplest amido
[illegible]
Naller obtained from the decomposition
of β diazo naphthalene nitrate in alcohol
principally β naphthoe ethyl ether
$C_{10}H_7 \cdot O \cdot C_2H_5$,
and but a small quantity of the
hydrocarbon Naphthalene

Fluorine

This substance was first obtained by Gay-Lussac and [illegible] ethyl iodide and anhydrous hydrofluoric acid, and it was called by him hydrofluoric ether. Dumas obtained it in the same way, and by the same method. He called it Fluorine. [illegible] the formation of this fluoride ether, in the literature is by these two investigators. [illegible] 1760, [illegible] 1787, [illegible] the [illegible] the [illegible] [illegible] [illegible]

point to [illegible] from [illegible]
[illegible] the [illegible] [illegible] [illegible]
[illegible] [illegible] [illegible] the diazo
[illegible] sulphate was made.
Both were found to boil
[illegible] at 150°C. [illegible]
thermometer [illegible] a standard one?
[illegible]
[illegible]
[illegible]

the phenetol, made from the decomposition of the diazo compound, agrees exactly with the description of Cahours. Unlike [illegible] it does not solidify even when cooled down to −20°C. When treated with fuming nitric acid, dinitro-phenetol is very readily formed. This dinitro-phenetol melts at 86°-87°, and resembles somewhat the dinitro-benzene, which melts at 89°. As Griess obtained a compound, melting at 84°, on treating the [illegible] with fuming nitric acid, he [illegible] dinitro-benzene [illegible] and which [illegible] of the fuming [illegible]

since if [illegible] only a trace of meta nitro benzene is formed in this reaction, phenetol being the principal product, [illegible] dinitro phenetole and a little [illegible]

[illegible]

0.2420 gm. phenetol gave 0.6351 gm. CO_2 = 0.6315 gm. C
[illegible] gm. H_2O [illegible]

Found	$C_6H_5-O-C_2H_5$
71.11% Carbon	71.86%
8.00% Hydrogen	8.19%

The Normal Diazo Alcohol Reaction

Having obtained phenol, as the principal product of the action of alcohol on diazo benzene nitrate, and as no good explanation of this peculiar reaction could be found in the explanations to the normal diazo alcohol reaction, attention was turned to those amido compounds, which were on record as giving the Goldberg regular diazo alcohol reaction. It was hoped that these amido bodies would exhibit some regularity, in the position of the groups in the molecule, other characteristic, which would account for the cause of this

diazo

had given

—, through the Griess

reaction were col-

and arranged in order,

beginning with those containing

substituting groups in the

same item those with 3, 4, 5.

Amido Compounds containing two Groups

Schmitt, Annalen 120, 153, found that

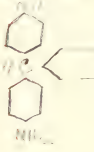
diazo compound from para-

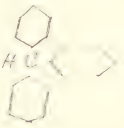
gave benzene sulphonic acid.

The odour of aldehyde, using the para-

that the yield of benzene-sulphonic acid is very satisfactory. In this connection should be mentioned Kinzlberger's work on the [illegible] from meta-nitro-benzene-sulphonic acid with alcohol to [illegible] an acid, which, on being worked into the [illegible] will not have a constant melting [illegible] sulphanilic. Different crystalline modifications of this substance melting [illegible], the melting point of the purest benzene sulphonic being 156°, (Ber. Oberreth Annalen 221, 206).

hydrocarbon, diphenylmethane from triphenyl-diamido-triphenyl methane, (Leucaniline), through the [illegible]





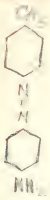
[illegible] grams were obtained, however, [illegible] 300 of the Leucaniline. Fischer, (Ann. Chem. Soc. 20, 471), decomposed the diazo compound from Benzidine, (para-diamidodiphenyl), with alcohol and obtained diphenyl

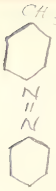
Fischer, Annalen 206, 471, found that diamidotriphenyl methane, [illegible] the amido groups are on-

the para position to carbon, gave triphenyl [illegible] by the diazo chemical reaction.

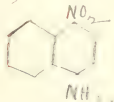
Meldola and Hewitt, (Journal the 12, 1402), made diphenylenamine from para diamido-diphenylamine, by the diazo reaction.

[illegible], obtained [illegible]-azo-benzene [illegible] from [illegible]-azo [illegible] by the diazo chemical reaction.

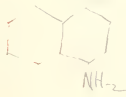




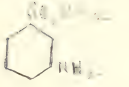
Beilstein and Kurbatow, (Annalen 160, 87), obtained mononitro-naphthalene $\alpha_1 \alpha_2$ nitronaphthylamine, by means the diazo alcohol reaction.



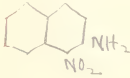
Rather, (Berichte 17, 950), obtained a brom-naphthalene from β brom-α naphthylamine by same reaction.



Hubbenette, (Annalen 221, 205),

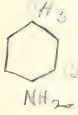


Jacobson, (Berichte 14, 1792) obtained
α nitronaphthalene from α nitro α
naphthylamine by same reaction.



have

have



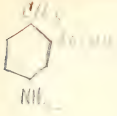
2/3 of the Thiocarbamic acid.

Vallin, B. 19, 2952
Von Pechmann, B. 7, 711; A. 173, 201

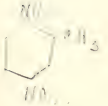
Beilstein and Kulberg, A. 155, 24.
Zincke's Nitrosation, 70% yield

Probenius, B. 7, 1062.
Weil N.O also Z. f. Chem., 164; Gmelin IV XVIII, 2704

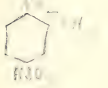
Acetic, A. 161, [illegible] 172, 335
Reimann-Phelps, Am. Ch. Jour., 4.

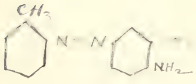


Hoffken, A. 221, 209.

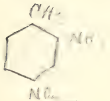


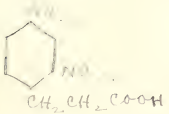
Bilstein und Kulberg, A. 158, 346





Schulz, B. 1, 470



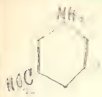


Trowbridge, A. 161, 173.

Limpricht, B. 18, 1402

Laiblin, A. 173, 62.

Nölting A. 190, 44.

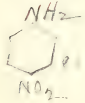


Hübner, B. 10, 1703

Böckin, B. 10, 1703

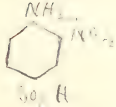
Beilstein + Kurbatow, A. 182, 90.

Beilstein + Kurbatow, A. 182, 97.



Beilstein + Kurbatow, A. 182, 107.

[illegible]



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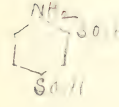

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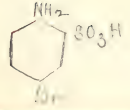

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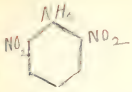
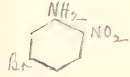
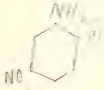


Salkowski, A. 171, 271

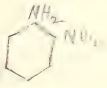
is heated twice at 130° with chlorobenzene.



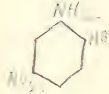
Stuhlmann, 1910, 1704
Körner, J. 1870, 344

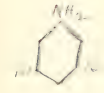


Griesheim-Elektron, A. 182, 101



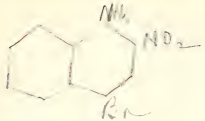
Griesheim-Elektron, A. 172, 105.





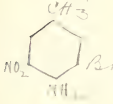
Körner, J. 1870, 344.

Meldola, B. 17, 1961

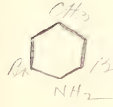


Liebermann, A. 113, 260

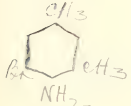
Amido Compounds containing Chlorine



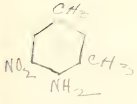
Tchelincheff, A. 197, 202



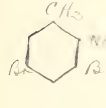
Tchelincheff, A. 164, 188.



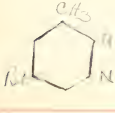
Tchelincheff, A. 197, 215.



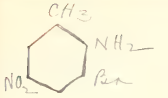
Tchelincheff, A. 207, 94



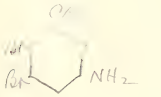
Tchelincheff, A. 197, 197.



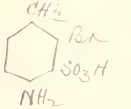
Tchelincheff, A. 197, 207.



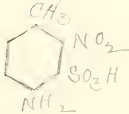
Neville & Winther, B.13, 964.



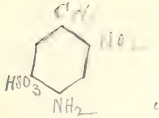
Neville & Winther, B. 13, 964



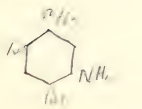
Von Pechmann, A.173, 212



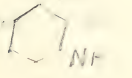
Von Pechmann, B.7, 72 0
A.173, 214.



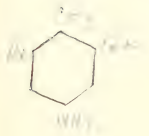
in a sealed tube at 100°. With Na + alcohol ethers,

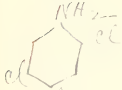


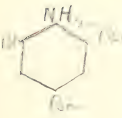
Neville & Winther, B13, 971.

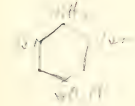


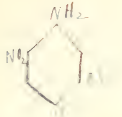
Neville & Winther, B.13, 971



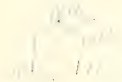


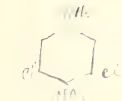




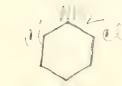


Beilstein 4, 1060, A.1 (6) 231

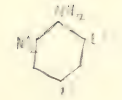


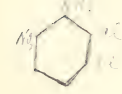


Beilstein 4, 1060, A.1 (6) 231

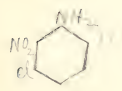


Körner, A. 137, 32

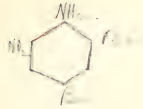


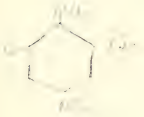


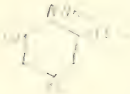
Beilstein and Kurbatow, A. 138, 351

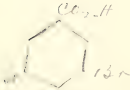


Beilstein 4, 1060, A.1 (6) 231

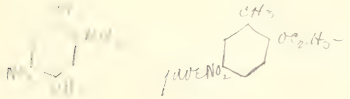




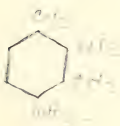




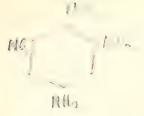
Beilstein V, 1078, Anm. 4



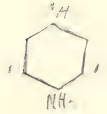
Cadenbach, B. I, 1212.



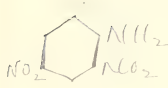
Strecker, B. 17, 2425



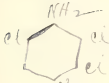
Beilstein, B. 13, 243



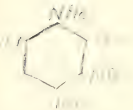
Leitmann, Klotz, A. 231, 322



Skraup, A. 217, 183.



Beilstein & Kulberg, A. 176, 236.



Körner, J. 1876, 347.

Körner & Contardi, 1893, 975.

From this survey of the amido compounds, yielding the regular diazo-reaction it will be seen, that the [illegible] group is most likely to be replaced by hydrogen, when its diazo compound is decomposed with alcohol. When we remember that

in the case of the diazo compounds, yielding ethers of phenols, the amid group generally occupies the ortho- position [illegible] seems to be more [illegible] of the replacement of the NH_2 group by hydrogen, the thought suggests itself, notwithstanding the insufficiency of the data, and the fact that most of these reactions have only been carried out in a few cases, and that [illegible] of the amid group in the meta, [illegible] to the other groups, in general the diazo diazo reaction, determining whether the diazo group will be replaced by hydrogen, or by the ethoxy groups. With this thought

Ortho-Diazo-Amino-Sulphate

25 grams of pure ortho toluidine, acetic compound m. pt. 106°, were dissolved in [illegible] and an excess (25 grams) of concentrated [illegible] acid. Heat is then applied until all the [illegible] solution. The flask containing the aqueous solution of the toluidine sulphate, and [illegible] nitrite [illegible] the [illegible] of the [illegible] nitrite [illegible] oxide. The action is [illegible]

the diazo sulphate is placed upon
drying paper, and the ether al-
lowed to evaporate at the temper-
ature of the room. The white
[illegible] green, when washed with

Abount 50 grams of the dry ortho-
diazo-thiocresol sulphate were placed
of absolute alcohol added, the
flask connected with an inverted
condenser, and gently heated on a water

decomposition begins. Nitrogen is
given off, but no odor
the earlier experiment, it was found
best to conduct the decomposition
at as low a temperature as possible
in order to avoid tarry products.
After most of the nitrogen
heated to boiling to insure complete
decomposition
a water bath, and diluted with
about six times its volume of
an air free to the exclusion of the
and dried over fused calcium

chloride and found to boil at 170°.
Hence not toluene but ethoxytoluene
or the ethyl ether of ortho-cresol. Only [illegible]
[illegible] alcoholic distillate.
[illegible] oil as the alcohol,
water was added & the mixture
distilled in steam. With the steam
lighter than water, and found
identical with the oil
from the alcoholic distillate. The
oil on being separated, washed with cold
soda solution, then with water,
was found to boil at 174° (corr.), and
had the general properties of
ethoxy toluene or (o)-cresol-ethyl ether,
(B.H., 24(A.), 217, 41). With nitric acid
it yielded a nitro compound melting

[illegible] ... [illegible] ... [illegible] ... [

Para-Diazo-Toluene Sulphate

25 grams of the pure crystallized para-toluidine [illegible] at 147°; were dissolved in about 250 c.c. of ordinary alcohol and an excess 25 grams of sulphuric acid gradually added. Heat was then applied until all the para toluidine sulphate was dissolved. The flask is then placed in ice water and a rapid current of nitrogen trioxide from arsenic trioxide and nitric acid [illegible]. Diazo-toluene sulphate crystals begin to form after a time in [illegible] when the nitrogen trioxide ceases to be absorbed.

Action of Alcohol on Para-Diazo-Toluene Sulphate

diazo compound, as well as the

10 grms of the para-diazo-tol-
sulphate were then decomposed,
the residues united, and the
alcohol distilled off from a
water bath. The alcohol dis-

[illegible] This oil was isolated, was [illegible] calcium chloride, and subjected to fractional distillation. Obtained two fractions. The first was a colorless oil, lighter than water, which smelled like [illegible] which boiled at 110°. The second fraction was colored slightly [illegible] liquid. Water was added to the fraction flask, and the [illegible]

[illegible] washed, dried over [illegible] and distilled, it boiled constant at 186°-187°4 - is hence the Ethyl-Ether of para-cresol

$$C_6H_4 \begin{cases} CH_3 \\ OC_2H_5 \end{cases} (1)$$

Cp. Beilstein 2, 624 & Fait 186, 1.

Oxidised a grams of this Ethoxy-[illegible] with permanganate, and obtained para-Ethoxy-benzoic acid melting at 195° (Cader berra A. 141, 204). There can [illegible] the para-ethoxy toluene or [illegible] the residue left is the [illegible] which was neutralised with Barium carbonate, filtered [illegible]

$$C_7H_7N_2HSO_4 + C_2H_6O = C_7H_8 + C_2H_4O + H_2SO_4 + N_2$$

The para-ethoxy-toluene was [illegible] the Equation

$$C_7H_7N_2HSO_4 + C_2H_5OH = C_7H_7OC_2H_5 + H_2SO_4 + N_2$$

[illegible] were obtained, i.e. 18.1% of the theoretical yield. From a [illegible],

Toluene, 43.6% yield
Ethoxytoluene 18.1% "

it is seen that the tendency of para-diazo-toluene sulphate, when decomposed in alcoholic, is to form the hydrocarbon, by the replacement of the amido group by hydrogen. This tendency is still more marked in the case of derivatives of para-tolu[illegible]dine, in which the substi-

[illegible] reaction [illegible]
Corack obtaining a 70% yield
of the hydrocarbon reaction,
with m-nitroparatoluidine.
Having been shown that the ortho-
toluidine yields 50.5% ortho-ethoxy-
toluene, while the para compound
gives 43.6% toluene and 15.1% para-
ethoxy-toluene, in the decomposition
of their respective [illegible]

Action of Ethyl Nitrite on Methyl Iodide

25 grams of the above bis nitroso [illegible]
[illegible] and about 250 cc. of a
strong absolute alcohol solution
of ethyl nitrite added; the flask
connected with a long inverted
condenser. Nitrogen begins at once
to be evolved, and after standing
[illegible]

[illegible] Hence 6.7% of the [illegible]

The meta-nitro-toluene was [illegible] with chromic chloride and the [illegible] acid and the [illegible] obtained.

Meta-Diazo-Toluene Sulphate

If grams of the metatoluidine were [illegible] absolute alcohol, excess of concentrated Sulphuric acid [illegible] diazo [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] [illegible] exposed to the air. This diazo compound was filtered off, washed with absolute alcohol, [illegible]

ethoxy toluene with potassium permanganate and obtained meta-ethoxy-benzoic acid, melting at 132°. (Ber. d. chem. Ges., 13, 111; Annalen, 153, 333.)

10 grams of the ethyl ether of this meta-cresol were obtained from the 15 grams of meta-toluidine used, and no toluene. The decomposition of the meta diazo toluene sulphate in alcohol is represented by the equation

$$C_7H_7N_2HSO_4 + C_2H_5OH = C_7H_7OC_2H_5 + H_2SO_4 + N_2$$

40% of the theoretical yield were obtained. Here as in the case of the ortho toluidine the predominant reaction is the one yielding the phenol ether

The results obtained with the three toluidines are therefore:

orthotoluidine — 50.5% o) ethoxy toluene + 49.5% toluene

meta toluidine — 40.9% m) ethoxy toluene + 59.1% toluene

paratoluidine — 43.6% toluene + 56.4% p) ethoxy toluene.

These results should be compared with those obtained by Hroblewsky, with the three monochloraniline, [illegible] are in perfect accord. The only chlor-toluidine [illegible] giving the reaction, or [illegible] the reaction [illegible] the ortho- [illegible] paratoluidine.

$$\left\{ \begin{array}{l} (NH_2 = 1) \\ 4 \\ (NH_2 = 1) \end{array} \right.$$

on which the amido and methyl groups occupy the para position with respect to each other. The [illegible] made from the [illegible]

...ine acridine as that from the para chlor
meta toluidine, both gave ethoxy com-
pounds, water decomposed in alcohol.
In these two chlor toluidines it will
be noted the methyl and amido
groups occupy the ortho + meta posi-
tion, [illegible]
[illegible]
[illegible]
[illegible]
[illegible] toluidine has.

The results of Ladenburg with ethyl
toluene diamine (see page 44) [illegible]
[illegible]
[illegible]
[illegible]
[

[illegible] found [illegible]. In the course of the [illegible] the normal, or [illegible] [illegible], it was shown, that [illegible] compounds, containing paraffin residues, [illegible] contain the paraffin and amido groups in the ortho [illegible] to each other; whereas, in the case of those amido compounds on record, as giving the normal [illegible] found to uniformly occupy the para position, relative to [illegible]; such [illegible] obtained with the three Isomides. [illegible] the three sets of compounds, [illegible] the [illegible], [illegible] amido compounds containing paraffin

residues, the position of the amido group in the product depends on whether the original amido compound, in which the amido group occupies the ortho, or the meta position to the paraffin residue, the abnormal or ethoxy reaction predominates. When however, the amido group occupies the para position the alcohol reaction yields principally the hydrocarbon in accordance with the well known equation of Griess.

A New Nitration

[illegible] were [illegible] prepared by [illegible] to determine the relative amounts of [illegible] and [illegible] formed in the decomposition of [illegible] in [illegible], it was noticed that only nitro-phenol was [illegible] formed, and in considerable quantity. It is to be [illegible] that [illegible] in this way. Even in the [illegible] [illegible] the [illegible] was practically absent, [illegible] hardly [illegible], that phenol was first formed, and that the ortho-nitro-phenol resulted from the action of the free nitric acid

this. The idea then suggested itself, that we were have to deal with a case of molecular rearrangement ("molecular transposition"), if we replace the diazo-group in the diazo benzene nitrate

$$C_6H_5-N_2-NO_3$$

we have left

$$C_6H_5-NO_3$$

and this contains the elements C_6H_5OH [illegible] from [illegible] to [illegible]. We [illegible] transposition expressed by the Equation:

$$C_6H_5-N_2NO_3 = N_2 + C_6H_4\begin{matrix}NO_2(O)\\OH\end{matrix}.$$

In order to test this hypothesis, we hydrolyse ortho-nitro diazo benzene nitrate with which the diazo benzene nitrate does not [illegible]

1.) 15 grams of the dried diazo-benzene nitrate (made & dried in the usual way, were placed in a 500 c.c. florence flask, and 200 c.c. of anhydrous toluene, (dried over sodium), added. The flask was then placed in a water bath, and the bath gradually heated. The [illegible], and the temperature of the bath kept as low as possible to accomplish the decomposition. The diazo benzene nitrate soon began to give off Nitrogen, & was converted into [illegible] requiring a deep red color. An excess of a solution of sodium carbonate is then added to the toluene. The toluene [illegible] is then separated by the sodium car-

[illegible] and distilled with steam. A yellow [illegible] was recrystallized from alcohol and found to melt at 45°, in all the [illegible] and general properties of [illegible] ortho- [illegible] was obtained from 15 grams [illegible] diazo benzene nitrate [illegible] 24% of the diazo benzene nitrate [illegible] equation

$$C_6H_5-N_2NO_3 = N_2 + C_6H_4\begin{matrix}OH\\NO_2\end{matrix}(1)$$

The residue left in the retort, from [illegible] ortho [illegible]

and mass remaining, combining was then
sodium sulphate examined for
para-nitro-phenol. Not even a trace
of this was found.

[illegible] benzene
nitrate were then decomposed in-
[illegible] ortho nitro phenol
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible]
[illegible] ortho
nitro phenol [illegible]
[illegible]
[illegible]
[illegible]
decomposition in an analogous man-
ner yielding phenol orthosulphonic
acid [illegible]

$C_6H_5\text{-}N_2HSO_4 = N_2 + C_6H_4 \begin{cases} H \\ HSO_3 \end{cases}$ (1:4)

the toluene separated. The solution was then boiled to free it entirely from [illegible], and evaporated to dryness. The salt left, which consisted mostly of potassium sulphate, was treated with alcohol to remove the [illegible] and evaporating this alcoholic solution [illegible], leaving the usual appearance of the [illegible] crystals. The solution from which the crystals separated gave a violet color with ferric chloride. 0.2742 grams of salt gave 0.1044 K_2SO_4 which corresponds to

[illegible] 18.05% K. 18.43% K

This result will be used to [illegible] for the potassium salt of toluene

sulphonic acid $\frac{1}{2}$ HBr $\xrightarrow{Cl_2 + KClO_3}$ as it does

But all attempts to make a sulphamide by treating this potassium

and ammonia, Kailed, and this

taken in connection with the color

reaction decides in favor of the

the potassium ferrosulphonate

2. In another experiment 1½ grams

of dibenzene sulphate were

decomposed in anhydrous toluene

the temperature of the bath being kept

at 90°C. Added water and barium

carbonate. Poured off the toluene

solution and some

time.

animal charcoal for some time.
Filtered and added solution of
[illegible]
[illegible]
[illegible]
[illegible]
excess
hours [illegible]
and potassium — Ethyl phenol
sulphonate was formed according
to the equation

$C_6H_4 \begin{cases} OH \\ SO_3K \end{cases} + C_2H_5Cl$ [illegible]

[illegible]
[illegible]
[illegible]
Ether to dissolve out the [illegible]
[illegible]

in water and a slight excess of

water, thus formed is a transparent

in hot water and almost insoluble

The [illegible] gram

$BaSO_4$

21. 0.1402 grams gave 0.1377 grams $BaSO_4$

which corresponds to

II 19.70 % Ba } 19.74 % Ba 19.80 % Ba

I 19.77 % Ba

[illegible] sulphate [illegible] decomposes in toluene in exactly the same way the nitrate does. We may suppose the orthosulphonic acid [illegible] passes over into the [illegible] compound [illegible]

The attempt was made to decompose the diazo-toluene sulphate, as well as the [illegible] in the same manner. Decomposition [illegible]

Summary

The results described in the preceding [illegible] may be summed as follows:

1. [illegible] diazo-aceto reaction on record, show that [illegible] 24 amido compounds, 13 contain paraffin residues and that 11 of these 13, contain the amido group and paraffin group in the ortho position to each other.

2. The principal product of the reaction of nitrous acid on both diazo-benzene nitrate and sulphate is phenol.

Benzene is also formed but in small quantity. Similar results have also been obtained in the case of the naphthalene sulphates

3. The close study of the amido compounds on record, which yield the hydrocarbon by the decomposition of the diazo compound with alcohol, shows that a majority of these compounds contain the amido group in the para position to the methyl group in the molecule.

4. The principal product of the action of alcohol on ortho diazo-toluene sulphate, is the ortho-, with small quantities of meta-diazo-toluene sulphate

the ethers of meta-

sulphating, it is

These results

From all above facts the following conclusions seem to be justified:

1. That the

reaction is the one yielding the ethers of phenols according to the general equation

$$RN_2HSO_4 + C_2H_5OH = R.OC_2H_5 + N_2 + H_2SO_4$$

2.

decomposition which takes place but proceeding to a much less extent. It is, however, the prevailing